Magnetic field-induced transitions in geometrically frustrated $Co_3V_2O_8$ single crystal

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(Received 21 September 2005; revised manuscript received 27 January 2006; published 21 March 2006)

Magnetization and specific heat of the $S=3/2$ antiferromagnet on a kagome staircase, $Co_3V_2O_8$, were investigated as a function of temperature and magnetic field. The low temperature magnetization data revealed unusual features related to the strongly frustrated spin lattice. Of particular interest were magnetic field induced phase transitions observed for various orientations of the magnetic field. Abrupt macroscopic magnetization jumps induced by a magnetic field directed along the ***c***-axis have been observed below 6 K. This effect was also observed for a high enough magnetic field applied in the ***a***-***c*** plane. It is suggested that the jump, observed for $H\|\boldsymbol{c}$ is due to a spin reorientation phase transition. It was shown that $Co_3V_2O_8$ crystals are characterized by a strong magnetocrystalline anisotropy of an easy-plane type. This anisotropy is due to the presence of Co^{2+} ions in octahedral positions.

DOI: 10.1103/PhysRevB.73.094425 PACS number(s): 75.40.Cx, 75.50.−y, 75.30.Kz, 75.25.+z

INTRODUCTION

Frustration in magnetism refers to the inability of a system to satisfy competing interactions and to find an unique ground state because of the geometrical constraints. Frustrated magnetic materials have recently attracted much interest, both theoretically and experimentally. This interest is stimulated by attempts to find new fundamental effects such as the magnetization plateaus[1–9] and the magnetization jumps,[10–13] which represent a genuine macroscopic quantum effect, as well as by new possible technical applications of these materials in the adiabatic demagnetization refrigerators due to their enhanced magnetocaloric properties.[14] The geometrically frustrated magnets exhibit complex ground states, e.g., spin liquid[15] or spin ice states.[16,17] Of particular interest has been magnetism on the two-dimensional kagome lattice which consists of corner-sharing triangles. This system is highly frustrated because of specific geometry and an interplay with strong quantum fluctuations. Recently, the isostructural compounds $M_3V_2O_8$ ($M=Ni,Co,Cu$) were shown to be new variants of kagome lattice.[18–23] In this case the planes that contain the edge sharing MO_6 octahedra are not flat (as in the regular kagome lattice) but buckled forming a staircase-like structure. These kagome-staircase magnetic layers are separated by the nonmagnetic VO_4 tetrahedra. As a consequence the geometric frustration is reduced allowing long-range magnetic order. The kagome-staircase system contains two types of crystallographically inequivalent magnetic sites for M^{2+} ions: The cross-tie sites (M_i) which form the apices of the isosceles (nearly equilateral) triangles and the spine sites (M_s), which form the bases of the triangles.

The most of the studies of the kagome-staircase magnetic crystals were devoted to the $Ni_3V_2O_8$. It was shown that for this compound a long-range ferroelectric and incommensurate magnetic order appear simultaneously in a single phase transition.[22] Moreover, the magnetic and ferroelectric orders are strongly coupled. Using thermodynamic and neutron data the magnetic phase diagram was established for $Ni_3V_2O_8$ single crystal.[21] The transition from a paramagnetic to a high temperature incommensurate (HTI) phase was shown to appear at $T_{PH}=9.1$ K. Then at $T_{HL}=6.3$ K this phase transforms into a low-temperature incommensurate (LTI) phase. Both phase transitions are continuous. Below $T_{LC}=3.9$ K the crystal displays two commensurate slightly different canted antiferromagnet phases (C,C'). The transition at T_{LC} from the LTI phase to one of these phases is discontinuous. Kenzelmann *et al.*[23] presented a mean-field phase diagram assuming only isotropic exchange interactions J_1-J_2 in the magnetic system (where J_1 and J_2 are the exchange constants between first and second nearest neighbors, respectively) and single-ion anisotropy. The diagram describes qualitatively the properties of $Ni_3V_2O_8$ crystals and because of its generality is probably also relevant for the description of phase transitions in $Co_3V_2O_8$ crystals.

The experimental data for $Co_3V_2O_8$ are much scarcer[18–20] than for its Ni-based counterpart. Magnetization measurements performed on polycrystalline $Co_3V_2O_8$ (Ref. 18) reveal that below 6 K this compound is ferromagnetic (FM) in character. Heat capacity data[18] show the presence of the phase transitions at about 6 and 11 K. The measurements on $Co_3V_2O_8$[20] single crystals reveal the presence of a large magnetic anisotropy in these compounds with the easy axis along the ***c***-axis and hard—along the ***b***-axis.

In this paper we describe results of magnetic measurements performed on $Co_3V_2O_8$ single crystals as a function of temperature and magnetic field. We concentrate on the differences between $Ni_3V_2O_8$ and $Co_3V_2O_8$, which have a similar crystal structures but different magnetic ions with spins $S=1$ and $S=3/2$, respectively. One expects to find considerable differences between the two compounds since the ground state of the Ni^{2+} ion is an orbital singlet whereas the ground state of Co^{2+} ion is an orbital triplet. Thus in the case of Co^{2+} one should expect a strong ion-lattice coupling and possibly also the crystal lattice deformations related to a Jahn-Teller effect which influences the character and magnitude of exchange interactions in the system.

EXPERIMENTAL

Single crystals of $Co_3V_2O_8$ were grown by floating zone technique using an optical image furnace. The crystal struc-

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TABLE I. Coordinates of ion positions in the $Co_3V_2O_8$ unit cell.

Position\Ion	Co(1)	Co(2)	V	O(1)	O(2)	O(3)
x	0	0.25	0	0	0	0.2672
y	0	0.1312	0.3788	0.2359	0.0065	0.1159
z	0	0.25	0.1216	0.2327	0.2283	1.0080

ture was investigated at room temperature by the powder x-ray diffraction method using a Siemens D5000 diffractometer with filtered Cu $K\alpha$ radiation and a high resolution semiconductor detector Si[Li]. The diffraction patterns were measured in the $\Theta/2\Theta$ scanning mode in the angle range 34°–116° with a step of 0.02° and an average time of 10 s/step. The experimental data were analyzed by the Rietveld refinement method using the R.A. Young DBWS-9807 package[24] that enabled us to take into account positional and thermal corrections, the scaling factor, zero shift, background parameter, Bragg-peak profile parameter, and extinction correction. The analysis was performed assuming full occupancy of ions positions in the unit cell. It was found that samples investigated are orthorhombic (space group *Cmca*) with lattice parameters: $a=6.034(7)$ Å, $b=11.488(8)$ Å, and $c=8.300(4)$ Å, which are near to the previously reported data.[18,25] Table I displays the positions of ions in the unit cell. Magnetic measurements were performed for temperature range from 2 to 300 K in the magnetic field up to 50 kOe using a commercial superconducting quantum interference device (SQUID) magnetometer (MPMS-5, Quantum Design). The specific heat capacity was measured by means of the relaxation method, using the heat capacity option of the commercial Physical Property Measurement System (PPMS, Quantum Design). These measurements were carried out both in $H=0$ as well as for several values of magnetic field (up to 5.5 kOe).

RESULTS

Figure 1(a) displays the low temperature dependence of magnetization, M(T), measured in $H=50$ Oe applied along three crystallographic axes for $Co_3V_2O_8$. One can notice that the $M_a(T)$ dependence shows several peculiarities [see Fig. 1(b)]. Analogous peculiarities, occurring at similar positions, are observed in the specific heat, C, vs T dependences for $Co_3V_2O_8$ with external magnetic field $H\|\boldsymbol{a}$ (Fig. 2). It seems that these peculiarities are connected with the magnetic phase transitions. As it was mentioned before it might be expected that the sequence of phase transitions in $Co_3V_2O_8$ might be approximately identified with use of the mean-field phase diagram presented in the paper by Kenzelmann *et al.*,[23] calculated with the assumption that there are only isotropic exchange interactions and single-ion anisotropy in the magnetic system. This leads to the conclusion that the peculiarity at 11.2 K corresponds to the phase transition from a paramagnetic phase (P) to a high-temperature incommensurate magnetic structure (HTI) at $T=T_{PH}$. As the temperature is further decreased, the system undergoes at $T_{HL}=8.8$ K a

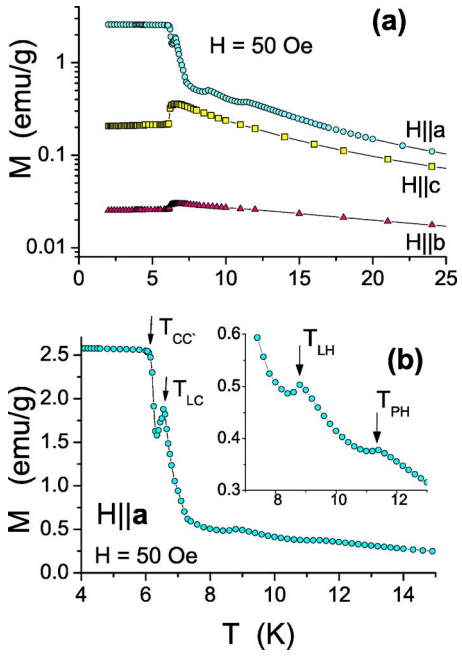

FIG. 1. (Color online) (a) The low temperature dependence of magnetization measured in $H=50$ Oe applied along three crystallographic axes for $Co_3V_2O_8$. (b) The pecularities in M(T) at low temperatures for $H\|\boldsymbol{a}$. The inset shows a part of the dependence in the enlarged scale.

second phase transition, this time to the next incommensurate magnetic phase: Low-temperature incommensurate magnetic phase (LTI). Subsequently, according to the mean-field phase diagram,[23] at $T_{LC}=6.6$ K this phase is transformed into an antiferromagnetic collinear commensurate phase (C), which—as the temperature is decreased still further transforms at $T_{CC'}=6.1$ K into another antiferromagnetic phase (C'). The transitions LTI-C and C-C' can be observed in magnetization measurements as well as in the specific heat (Fig. 2). One of these transitions ($T_{CC'}$) was previously reported by Rogado *et al.*[18] The above formulated model of the

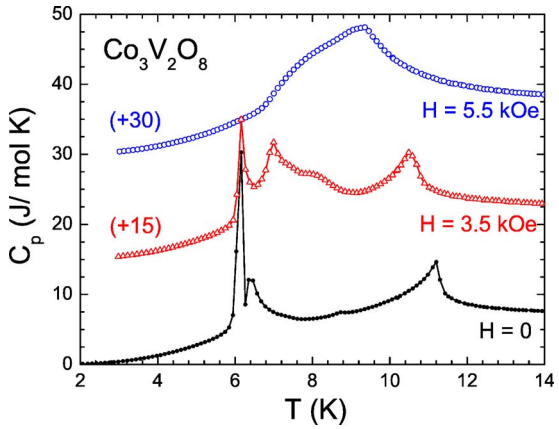

FIG. 2. (Color online) The specific heat of $Co_3V_2O_8$ at low temperatures in $H=0$ and for some values of $H\|\boldsymbol{a}$. Numbers given above the curves in parentheses are the values in J/(mole·K) by which the individual curves have been shifted along the C_p axis to avoid overlapping.

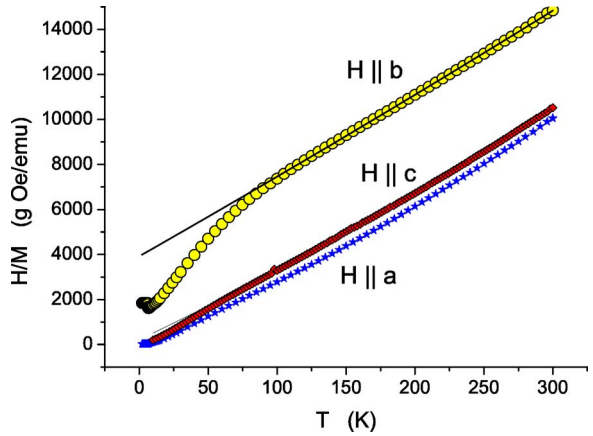

FIG. 3. (Color online) The inverse susceptibility vs temperature in magnetic field $H=0.5$ kOe applied along the $\boldsymbol{a}$, $\boldsymbol{b}$, and $\boldsymbol{c}$ axes. The solid lines represent the Curie-Weiss law fitting for temperature above 100 K.

magnetic structure of the respective phases based on the theoretical phase diagram[23] should be tested by means of the neutron diffraction measurements. At first glance another scenario is also possible. The very close location of T_{LC} and $T_{CC'}$ phase transitons may be related to the fact that there exist two subsystems of Co^{2+} ions: One corresponding to ions in cross-tie sites (Co_i) and second corresponding to those in spine sites (Co_s). Number of Co_s sites is twice that of Co_i ones. For $H=0$ these two subsystems are rather weakly coupled since the presence of the antiferromagnetically (AFM) ordered Co_s^{2+} ions produces a zero mean field on Co_i^{2+} ions in the Heisenberg nearest-neighbors exchange approximation.[21,23] It suggests that in the temperature region $T_{CC'}<T<T_{LC}$ the subsystem of Co_i^{2+} ions is in the incommensurate low-temperature phase. The Co_s^{2+} ions begin to transit to this phase at 6.6 K. With the increase of a magnetic field the both transitions should merge. However, the specific heat versus temperature (Fig. 2), measured for several magnetic fields, refute that hypothesis and confirm the existence of two phases: C and C'. The magnetization measurements results (not quoted here) are much more ambiguous, since the LTI-C transition becomes less pronounced and broadens with the increase of the field and finally disappears.

The anisotropy of magnetic properties observed at low temperatures arises since Co^{2+} ions in octahedral positions have a nonzero orbital moment. The nonzero orbital moment is also responsible for a significant anisotropy of the magnetic susceptibility at higher temperatures (Fig. 3). The temperature dependence $\chi(T)$ in wide temperature range (for $100\ \mathrm{K}<T<300\ \mathrm{K}$) can be well described by the Curie-Weiss law $\chi_i\ (T)=C/(T+\theta_i)$ with the paramagnetic Curie-Weiss temperatures equal to: $\theta_a=(-6.2\pm0.5)$ K, $\theta_b=(+114\pm3.5)$ K, $\theta_c=(+7.3\pm0.5)$ K, respectively. In the general case, paramagnetic Curie-Weiss temperatures θ_i are the sum of contributions from exchange interactions and crystal field.[23,26] For the system with isotropic Heisenberg exchange the contributions of these interactions to each θ_i are the same and equal to $\frac{1}{3}(\theta_a+\theta_b+\theta_c)$. On the other hand, for $Co_3V_2O_8$ crystals this contribution can be estimated from the measured θ_i values to be equal to 38.4 K. The differences between θ_i are determined by the crystal-field parameters (in frames of the single ion anisotropy model). These differences show that the system under consideration does not posses an easy axis anisotropy. Rather, they indicate the easy plane anisotropy with a smaller anisotropy which favors $\boldsymbol{a}$ over $\boldsymbol{c}$. A similar situation is seen in $Ni_3V_2O_8$. However, the differences between θ_i in $Co_3V_2O_8$ are two orders of magnitude larger than those measured in $Ni_3V_2O_8$, which confirms the above-formulated hypothesis that the main difference between the two compounds concerns the magnetocrystalline anisotropy. The contribution of exchange interactions to θ_i in $Ni_3V_2O_8$ is equal to 18.7 K so that it is lower than in $Co_3V_2O_8$. This correlates well with the differences in phase transition temperatures in both crystals, which indicates that the phase transitions LTI-*CiC*-C' may indeed be observed.

It has to be mentioned that the absolute value of the paramagnetic Curie temperature, θ_b, in $Co_3V_2O_8$ is significantly higher than the maximal ordering temperature, T_{PH}. The value of the ratio $|\theta_b/T_{PH}|$ determines the strength of a geometrical frustration.[27] The determined effective magnetic momement P_{eff} has values: $P_{eff}^{a}=(6.27\pm0.44)\ \mu_B/\mathrm{Co}$, $P_{eff}^{b}=(5.66\pm0.85)\ \mu_B/\mathrm{Co}$, $P_{eff}^{c}=(6.08\pm0.44)\ \mu_B/\mathrm{Co}$ noticeably larger than the prediction for a spin-only system ($3.87\ \mu_B/\mathrm{Co}$). It is probably due to the distinct orbital contribution to the overall moment. Similar observation was reported earlier.[18]

The low temperature heat capacity data are shown in Fig. 2. Besides the transitions at T_{LC} and $T_{CC'}$ described above, one could clearly distinguish for $H=0$ the transitions at $T_{HL}\sim8.7$ K and $T_{PH}\sim11.2$ K. It is also seen that the magnetic field applied along the $\boldsymbol{a}$ axis shifts some of the observed transitions to lower temperature (T_{PH}) or to higher temperature (T_{LC}), while no such effect is observed for $T_{CC'}$ in the applied fields. One of the important differences between our results and those reported for $Ni_3V_2O_8$ (Ref. 21) concerns the influence of magnetic field strength on positions of phase transitions (T_{LC} and T_{PH}). In $Ni_3V_2O_8$ these positions are practically independent of the field magnitude for the fields up to 10 kOe.

The influence of a magnetic field strength on a magnetization of the system was studied for three different field orientations: $H\|\boldsymbol{a}$ (Fig. 4), $H\|\boldsymbol{b}$ (Fig. 5), and $H\|\boldsymbol{c}$ (Fig. 6). Measurements of magnetization curves in $Co_3V_2O_8$ confirm once more that this material is characterized by a strong magnetic anisotropy and that the measured $M(H)$ dependences have a rather unusual character. One concludes from the data that the easy magnetization axis is directed along the $\boldsymbol{a}$-axis, whereas the hard axis is directed along the $\boldsymbol{b}$-axis. The same conclusions result from high temperature $\chi(T)$ measurements

Figure 4(a) presents the $M(H)$ dependences measured at several temperatures (2–30 K) in the magnetic field up to 50 kOe applied along the $\boldsymbol{a}$-axis. The magnetization curve at 2–6 K is typical of a FM phase. The value of saturation magnetization, M_S, close to $3\ \mu_B/\mathrm{Co}$ for $H\|\boldsymbol{a}$ suggests a collinear ferromagnetic ordering along the $\boldsymbol{a}$-axis. At temperatures between 7 and 12 K one can recognize some magnetic field induced peculiarities in the magnetization curves

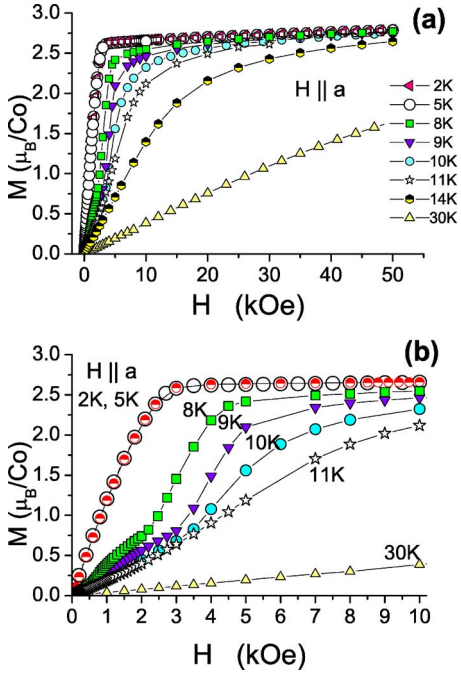

FIG. 4. (Color online) (a) The longitudinal magnetization measured at several temperatures (2–30 K) as a function of the magnetic field up to 50 kOe applied along the ***a***-axis. (b) The same dependences in a limited field range to expose better the pecularities arriving at $T=8-11$ K.

[see Fig. 4(b)]. It is the best seen at 8 K. The first part of M(H) up to about 0.5 kOe is linear, then there appears a bend and the magnetization begins to increase faster. In $H \approx 2$ kOe there is a next bend and the magnetization again starts to increase faster than previously with tendency to saturating for $H>4$ kOe. One could suggest that a first peculiarity (in 0.5 kOe) could be connected with the field induced transition of 1/3 Co^{2+} ions (probably located at Co_i sites) to a FM-like ordering and in 2 kOe the rest of Co^{2+} ions (located at Co_s sites) complete the transition of the whole system to FM ordering. It should be mentioned that

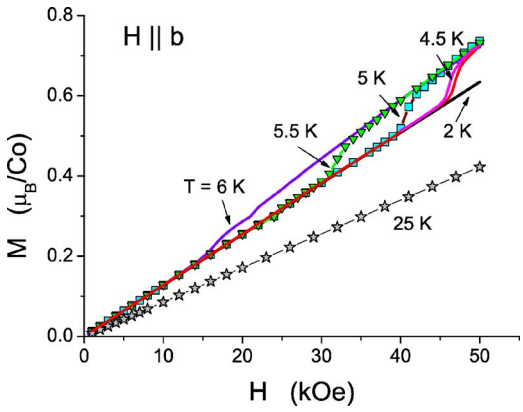

FIG. 5. (Color online) The longitudinal magnetization measured at several temperatures (2–25 K) as a function of the magnetic field up to 50 kOe applied along the ***b***-axis. At temperatures 4.5–6 K the magnetization jumps are well seen, with a critical field, H_{cr}, decreasing with an increase of temperature.

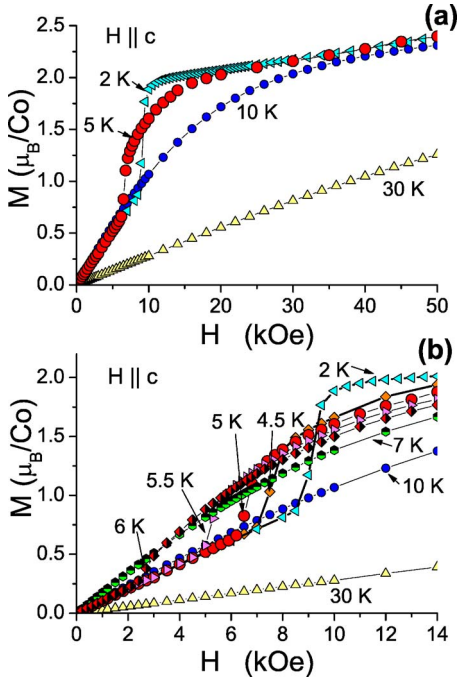

FIG. 6. (Color online) (a) The longitudinal magnetization measured at several temperatures (2–30 K) as a function of the magnetic field applied along the ***c*** axis. (b) The region of jumps in the M(H) dependences for $H \| \boldsymbol{c}$.

M($T, H=50$ kOe$\|\boldsymbol{a}$) is nearly independent on temperature up to about 12 K. At 23 K$\geqslant T \geqslant$12 K no peculiarities were found beside the tendency to saturation-like behavior and even at 30 K a small nonlinearity of M(H) for H up to 50 kOe was observed.

For $H \| \boldsymbol{b}$ (Fig. 5) the linear M(H) dependence at 2–4 K is typical of antiferromagnets. However, at temperatures 4.5–6 K the magnetization jumps are observed with a critical field, H_{cr}, decreasing with an increase of temperature. The critical field $H_{cr}(T)$ can be well approximated by $H_{cr}(T) \approx 82(1-T/6.1)^{0.43}$ [kOe]. We have also measured a transverse component of magnetization (along the ***a***-axis), which turned out to be comparable in amplitude to that along the H direction. Moreover, it has been found that after the jump (corresponding to the increase of M_b) the transverse component decreases. It should be noticed (see Fig. 5) that both before and after the jumps the M(H) dependences are linear and could be extrapolated within a range of error to M=0 in $H=0$. It suggests that both phases are purely antiferromagnetic without any spin canting effects. It is necessary to add that the jumps are characterized by the relatively narrow hysteresis. For the steepest transition at 4.5 K the width of hysteresis loop of $\Delta H \approx 600$ Oe was observed. This observation indicates that spin jumps are first order phase transitions.

Figure 6(a) presents the M(H) dependences measured at several temperatures (2–30 K) in the magnetic field applied along the ***c***-axis. Here the jumps are observed at the whole range of the lowest temperatures (2–6 K) for the field H <10 kOe [see Fig. 6(b)]. As the temperature is increased, the observed magnetization jumps decrease in magnitude and

they appear at lower fields. Moreover, no noticeable hysteresis was observed in these jumps. In the rough approximation a position of a jump could be described as $H_{cr}(T) = 10.5(1-T/6.1)^{0.3}$ (kOe). In the lowest magnetic fields, before the jump, the system behaves as an antiferromagnet. After the jump, the situation is quite different because the system is transferred to the ferromagnetic-like state. It seems, however, that it is not a transition of the standard spin-flop type, because external field is perpendicular to the easy axis.

DISCUSSION

Except for the differences between $Ni_3V_2O_8$ and $Co_3V_2O_8$ mentioned above, there are also other differences between these magnetic compounds. The main difference concerns the directions of the ferromagnetic moment, which for $Ni_3V_2O_8$ appears along the ***c***-axis, while for $Co_3V_2O_8$—along the ***a***-axis. It has to be stressed that in both cases the easy axis (direction of the antiferromagnetic vector) is directed along the ***a***-axis. The difference in the ferromagnetic moment direction (as well as in its amplitude) results from quite different mechanisms of their appearance. In the case of $Ni_3V_2O_8$ the Dzyaloshinskii-Moriya interaction leads to small canting of magnetic moments and consequently to the weak ferromagnetic moment along the ***c***-axis. In the case of $Co_3V_2O_8$ a low magnetic field applied along the ***a***-axis abruptly induces a transition antiferromagnet-ferromagnet with resulting ferromagnetic moment along the ***a***-axis. Similar transition in a quantum antiferromagnet was observed earlier on the kagome lattice.[5] The appearance of this transition was explained using the J_1-J_2 model on kagome lattice, with $(J_1 \times J_2) < 0$. The significant role here is played by the dimensionless parameter $\theta' = (g\beta H_{sat})/(k_B T_{max})$,[5] where T_{max} is a temperature of the broad maximum in the heat capacity C (T) (see Fig. 2) and H_{sat} is a saturation field. In our case $T_{max} \approx 11.2$ K could correspond to the transition temperature from the paramagnetic state to the high temperature incommensurate AFM state, which from the magnetic measurements in low magnetic field is determined to be about 11.4 K. A small value of the above defined parameter $\theta' \approx 0.12$ means that the system under consideration is in the vicinity of the boundary of the ferromagnetic phase. In this situation a transition to the ferromagnetic phase can appear in a quite low magnetic field.

For $H \| \boldsymbol{c}$ in the low field region the behavior is typical of an antiferromagnet. Since the field direction is perpendicular to the easy axis a magnetic field is not expected to induce the abrupt AFM-FM transition. Nevertheless, the magnetization jumps observed in magnetic fields between 10 and 3 kOe [for $T=(2-6)$ K, respectively] suggest that in part of the Co^{2+} ions (located in Co_s subsystem) the ferromagnetic state is induced. After the jump, for $H > H_{jump} = H_{cr}$, the Co ions located in the cross-tie positions (Co_i subsystem) are gradually aligning themselves ferromagnetically. Generally, such jumps can arise for different reasons. In the case of manganites and intermetallic germanide Gd_5Ge_4 the jumps were interpreted as the result of some kind of martensitic transformation associated with the strain between the phase separated (ferromagnetic and antiferromagnetic) regions.[28] It was also proposed that the formation of an inhomogeneous metastable state[29] or spin reorientation under the magnetic field[30] may lead to the observed magnetization jumps. An attractive theoretical explanation of the macroscopic magnetization jumps reported here is the hypothesis that they are due to local magnon excitations and represent a genuine quantum effect.[9–11,13] Unfortunately existing theoretical models, based mainly on the exact diagonalization of the finite size lattices with $s=1/2$ and $s=1$ only, cannot be used for interpretation of our results. These models do not take into account the magnetic anisotropy existing in the system.

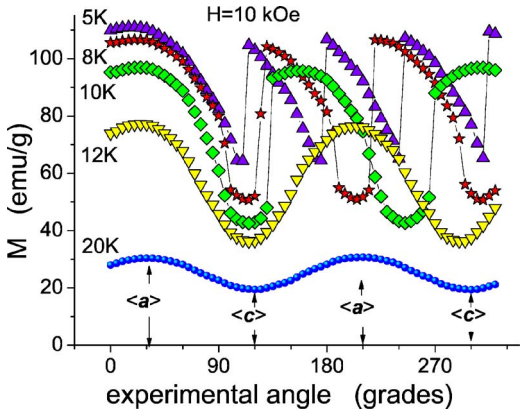

FIG. 7. (Color online) The magnetization vs a magnetic field orientation in the (***ac***) plane in $H=10$ kOe at several temperatures.

Moreover, the magnetization jumps predicted by the above-mentioned theory has not yet been observed experimentally in kagome lattices. In order to get more information on the macroscopic magnetization jumps, the measurements of magnetization in function of the magnetic field orientation in the (***ac***) plane have been carried out (see Figs. 7–9 as examples). A cascade of phase transitions has been observed induced by the change of magnetic field direction. The results lead to the conclusion that the jumps in this experiment appear at low temperatures only ($T<12$ K, i.e., in the magnetically ordered phases, both in commensurate phases, C

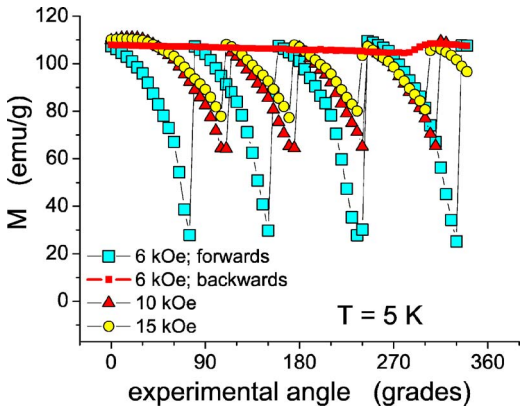

FIG. 8. (Color online) The magnetization vs a magnetic field orientation in the (***ac***) plane at 5 K for several values of the magnetic field strengths. For $H=6$ kOe, there is shown an example of irreversibility of magnetization on the direction of rotation (forwards and backwards).

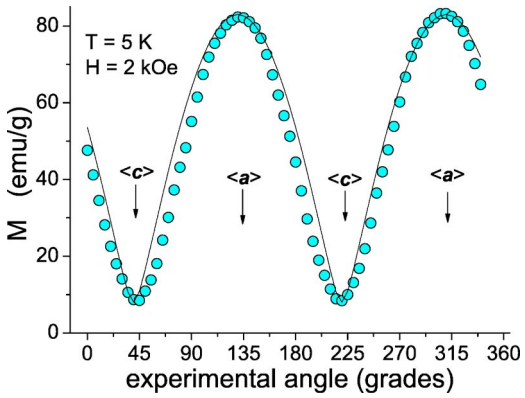

FIG. 9. (Color online) The magnetization vs a magnetic field orientation at 5 K for $H=2$ kOe as an example of $M(\alpha)$ for the field region, where the result is practically reversible for both directions of rotation. The solid line represents the fitting of the formula $M(\alpha)=H\cdot(\chi_{\|}{}^2\cos^2\alpha+\chi_{\perp}{}^2\sin^2\alpha)^{1/2}$ to the experimental data.

and C', as well as in incommensurate LTI and HTI phases) and in magnetic fields exceeding a critical value which depends on the temperature. Above $T>12$ K the dependence $M(\alpha)$, where α is an angle describing the magnetic field direction in the (ac) plane, is typical of paramagnets: It is determined by the anisotropy of g-factors [see in Fig. 7; $M(20\ \mathrm{K},\alpha)$ and just above the transition to the paramagnetic state $M(12\ \mathrm{K},\alpha)$]. In the ordered phase, in sufficiently weak magnetic fields, for which no jumps in magnetizations are observed, the $M(\alpha)$ dependence is determined also by the anisotropy of the magnetic susceptibility χ_{ij} (Fig. 9). Taking into account that both **M** and **H** vectors lie in the (***ac***) plane, the measured magnetization value should be given by $M(\alpha)=H(\chi_{\|}{}^2\cos^2\alpha+\chi_{\perp}{}^2\sin^2\alpha)^{1/2}$, where $\chi_{\|}$ and $\chi_{\perp}$ stand for the magnetic susceptibility in the direction, respectively, parallel and perpendicular to the ***a***-axis. The values of susceptibilities $\chi_{\|}$ and $\chi_{\perp}$ may be obtained from magnetization curves measured in the ***a*** and ***c*** directions [Figs. 4(b) and 6(b)]. The values of $M(\alpha)$ thus obtained are successful in describing the experimental data (see as an example Fig. 9). The change of direction of rotation of magnetization vector ***M*** does not show any hysteresis. When the magnetic field exceeds a critical value, the magnetization jumps back to the value close to the initial one. Equating the magnetic energy of the system before the jump

$$-\tfrac{1}{2}\chi_{\|}\cos^2\alpha H^2-\tfrac{1}{2}\chi_{\perp}\sin^2\alpha H^2+K\sin^2\alpha$$

[where K is an uniaxial in-plane anisotropy constant in the (***ac***) plane] and the energy after the jump

$$-\tfrac{1}{2}\chi_{\|}H^2+K$$

one can obtain the value of the critical angle α_{cr} at which the jump takes place

$$H^2(\chi_{\|}-\chi_{\perp})tg^2\alpha_{\mathrm{cr}}=2\ \mathrm{K} \qquad (1)$$

The jumps for the field in the (***ac***) plane appear not only in the vicinity of $H\|\boldsymbol{c}$, but also in a wide range of directions. This range, as well as the amplitude of the jump, depends on temperature and the magnetic field strength. These observations are in a qualitative agreement with Eq. (1)—with the increase of the applied field, the critical angle α_{cr} decreases (Fig. 8). Moreover, there is a strong hysteresis induced by the change of direction of rotation. This is related to the fact that magnetization jumps show the character of a first-order phase transitions. Although Eq. (1) defines the point where the energies of both phases are equal, it does not mean that in that point one phase will be transformed into the other: The precise point of transition is located in the phase coexistence region and depends on the seeding conditions of the new phase. In that way one can explain the deviations from the condition $M(\alpha)=M(\alpha+\pi)$.

The results of $M(\alpha)$ measurements can also elucidate the nature of the magnetization jumps for $H\|\boldsymbol{c}$, which is different than in manganites or intermetallic compounds. Namely, during the rotation of magnetic field in the ***ac*** plane there occurs a reorientation phase transition, which—for weaker fields—is a second order phase transition in which magnetization vectors are rotating from ***a*** to ***c*** axis. As the angle α is further increased, the second order phase transition becomes the first order phase transition with an associated magnetization jump.

In the case of the magnetic field oriented along the ***b***-axis, at temperatures 2–4 K and in the accessible field range ($H\leqslant 50$ kOe) the dependence $M(H)$ is typical of an antiferromagnet. The jumps are observed at somewhat higher temperatures (4.5–6 K) and have quite a different origin than that of jumps observed in the (***ac***) plane. As results from the neutron diffraction performed for $Ni_3V_2O_8$ (Ref. 21) in the absence of external magnetic field the antiferromagnetic vector, ***l***, is not strictly parallel to the ***a***-axis, but makes a small angle with it. It seems that this effect is present also in $Co_3V_2O_8$ and this explains an origin of jumps observed for $H\|\boldsymbol{b}$. Application of magnetic field $H\perp\boldsymbol{a}(H\|\boldsymbol{b})$ induces a magnetic moment ***f***. Its components are measured as longitudinal and transverse moments for $H\|\boldsymbol{b}$. In sufficiently strong magnetic field, in order to decrease the Zeeman energy one of the antiferromagnetic sublattices reorients leading to the alignment of ***l*** parallel to ***a***. This leads as a consequence to a jump of the longitudinal component of ***f*** and disappearance of its transverse component. It is in agreement with a behavior of the two components measured for $H\|\boldsymbol{b}$ and described in the previous section.

CONCLUSIONS

The high-quality single crystals of the kagome staircase lattices, $Co_3V_2O_8$, have been grown. Specific heat and magnetization measurements have been carried out on these crystals as a function of temperature and magnetic field. The configuration $H\|\boldsymbol{a}$ was considered in details and the magnetic properties compared with those established for $Ni_3V_2O_8$. The obtained results suggest that the sequence of phase transitions in both compounds is similar, even though the temperatures of these transitions are different. It has also been shown that the magnetic anisotropy in $Co_3V_2O_8$ is much larger than that in $Ni_3V_2O_8$. The unusual phase transitions induced by magnetic field were observed in $Co_3V_2O_8$

for various orientation of the field. In particular, the macroscopic magnetization jumps were observed for magnetic field in the ***a*-*c*** plane which seem to be due to reorientation of magnetization **M**. Magnetic field induced phase transitions were also observed for $H \| \boldsymbol{b}$ and $H \| \boldsymbol{c}$. In both cases, the phase transitions are of spin-reorientation type. The studies on magnetic properties of $Co_3V_2O_8$ have shown that this compound is a strongly anisotropic magnet of an easy plane type with a hard magnetization axis perpendicular to the (***ac***) plane. A strong magnetocrystalline anisotropy is related to the presence of Co^{2+} ions in octahedral positions.

ACKNOWLEDGMENTS

The work was supported in part by the Polish State Committee for Scientific Research (KBN) under the project 1 P03B 038 27. The authors are grateful to P. Aleshkevych for discussions and B. Krzymańska for technical assistance.

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